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The Reaction of Diethyl Acyl Phosphites with α,β-Unsaturated Carbonyl Compounds

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Synopsis. Diethyl acetyl and diethyl benzoyl phosphites reacted with propenal and 3-buten-2-one to give 1,4-addition products respectively. While the reaction of diethyl acetyl phosphite with 2-butenal and 2-methyl- and 3-phenylpropenals gave 1,2-addition products exclusively.

Trialkyl phosphites are known to react sluggishly with aldehyde. The reaction requires rather drastic conditions or much long reaction time and give several addition compounds such as 1:1, 1:2 or 1:3 in relatively low yield.[1] Dialkyl trimethylsilyl phosphite reacts smoothly with aldehyde and ketone to produce [α-(trimethylsiloxy) alkyl] phosphonate.[2] In the case of the reaction with α,β-unsaturated carbonyl compounds, the adducts resulting from 1,2 and 1,4 modes of addition have been obtained.[2] Diethyl acetyl phosphite (**1a**) reacted in diethyl ether exothermically with chloroacetaldehyde to give diethyl (1-acetoxy-2-chloroethyl)-phosphonate (56—95%).[3] Chloral, benzaldehyde, and 3-methylbutanal reacted also in same manner. The unchlorinated aldehyde required higher temperature.[4]

In this report, the reaction of diethyl acyl phosphite (**1**) with α,β-unsaturated carbonyl compounds is reported.

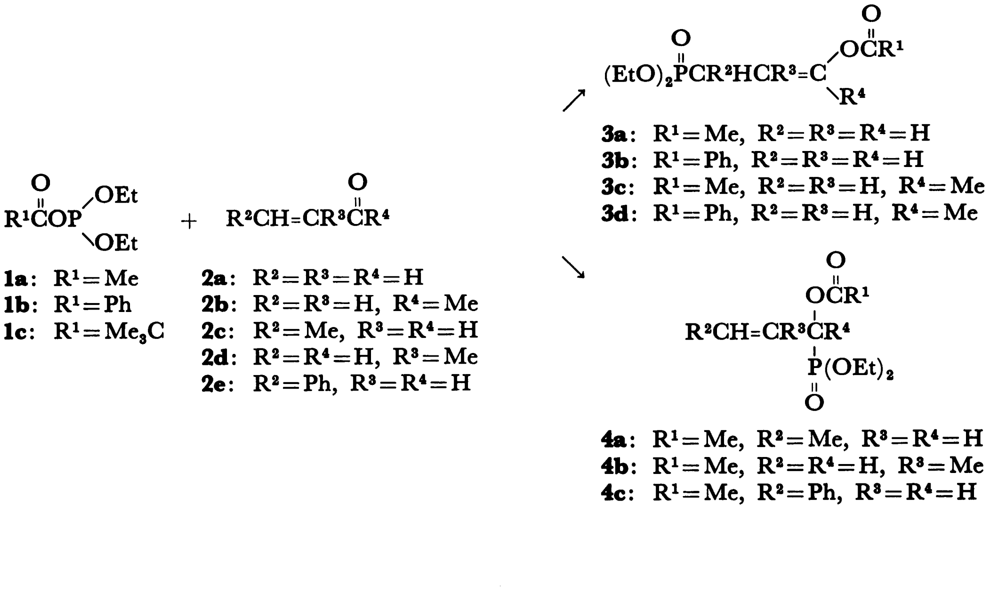
The reaction of diethyl acyl phosphite (**1**) with propenal (**2a**) proceeded exothermically at room temperature, while the reaction with α- or β-substituted α,β-unsaturated aldehyde (**2**) required heating to the refluxing temperature of benzene for several hours.

Propenal (**2a**) reacted with diethyl acetyl phosphite (**1a**) to give a mixture of 1,4-addition product (**3a**) and several unidentified products. In the case of the reaction of **2a** with diethyl benzoyl phosphite (**1b**), only 1,4-addition product (**3b**) was isolated in 69% yield. Diethyl 2,2-dimethylpropionyl phosphite (**1c**) did not reacted with **2a**. 3-Buten-2-one (**2b**) reacted also smoothly with **1a** and **1b** to afford only 1,4-addition products (**3c** and **3d**) respectively. On the other hand, when α- or β-substituted α,β-unsaturated aldehyde (**2c**, **2d**, and **2e**) was allowed to react with **1a**, only 1,2-addition products (**4a**, **4b**, and **4c**) were obtained exclusively. But 4-methyl-3-penten-2-one did not react with **1a**. Diethyl benzoyl phosphite (**1b**) did not react with these substituted aldehydes (**2c**, **2d**, and **2e**). Such a restricted limitation of the reaction may be caused by the high sensitivity of the dialkyl acyl phosphite (**1**) to steric hindrance. ^{1}H-NMR spectroscopy and GLC analysis of these products showed them to be in pure states, but assignment of olefin geometries could not be done.

Experimental

Dialkyl acyl phosphites were prepared from diethyl phosphorochloridite and sodium carboxylates.[5] Benzene was distilled under nitrogen from calcium hydride. Aldehydes and ketones were freshly distilled. All reactions were carried out under an atmosphere of nitrogen with the rigid exclusion of moisture from reagent and glasswares. ^{1}H NMR spectra were recorded on a JNM FX-100 spectrometer. Analytical gas chromatography were performed on a Shimadzu GC-7A gas chromatograph using a 2 m glass column of 2% OV-17 on a 60-80 mesh DMCS Chromosorb W support.

General Procedure. To a flask equipped with a reflux condenser, a magnetic stirrer, and an addition funnel were added 10 ml of benzene and 20 mmol of carbonyl compound. While the mixture was stirred at room temperature, 20 mmol of dialkyl acyl phosphite was added dropwise. After completion of addition, the solution was refluxed for 3 h. Distillation at atmospheric pressure removed the solvent. Susequent vacuum distillation afforded the product. The purity was checked by GLC analysis and ^{1}H NMR spectroscopy. The results are summarized in Table 1.



$R^1C(=O)OP(OEt)_2$ + $R^2CH{=}CR^3C(=O)R^4$

1a: $R^1=Me$
1b: $R^1=Ph$
1c: $R^1=Me_3C$

2a: $R^2=R^3=R^4=H$
2b: $R^2=R^3=H$, $R^4=Me$
2c: $R^2=Me$, $R^3=R^4=H$
2d: $R^2=R^4=H$, $R^3=Me$
2e: $R^2=Ph$, $R^3=R^4=H$

$(EtO)_2P(=O)CR^2HCR^3{=}C(OC(=O)R^1)R^4$

3a: $R^1=Me$, $R^2=R^3=R^4=H$
3b: $R^1=Ph$, $R^2=R^3=R^4=H$
3c: $R^1=Me$, $R^2=R^3=H$, $R^4=Me$
3d: $R^1=Ph$, $R^2=R^3=H$, $R^4=Me$

$R^2CH{=}CR^3C(OC(=O)R^1)(R^4)P(=O)(OEt)_2$

4a: $R^1=Me$, $R^2=Me$, $R^3=R^4=H$
4b: $R^1=Me$, $R^2=R^4=H$, $R^3=Me$
4c: $R^1=Me$, $R^2=Ph$, $R^3=R^4=H$

Table 1. Yields and physical properties of products (**3** and **4**)

Compd No.	Yield %	Bp °C/Pa	Formula	Found(Calcd)(%) C	H	P	^{1}H NMR, δ, in CDCl$_3$
3a	23	132—134/133	$C_9H_{17}O_5P$	45.15 (45.77	7.32 7.25	13.45 13.11)	1.32(6H, t, $J_{\mathrm{HH}}=7.1$ Hz, CH$_3$), 2.71(2H, ddd, $J_{\mathrm{HP}}=22.0$ Hz, $J_{\mathrm{HH}}=7.8$ Hz, $J_{\mathrm{HH}}=1.4$ Hz, PCH$_2$), 2.17(3H, s, COCH$_3$), 4.11(4H, quintet, $J_{\mathrm{HH}}=J_{\mathrm{HP}}=7.1$ Hz, OCH$_2$), 4.95(1H, ddt, $J_{\mathrm{HP}}=6.3$ Hz, $J_{\mathrm{HH}}=7.8$ Hz, $J_{\mathrm{HH}}=4.7$ Hz, -CH=), 7.18(1H, ddt, $J_{\mathrm{HP}}=6.9$ Hz, $J_{\mathrm{HH}}=$ 4.7 Hz, 1.4 Hz, =CHO)
3b	56	140—145/13	$C_{14}H_{19}O_5P$	56.23 (56.38	6.47 6.42	10.42 10.38)	1.30(6H, t, $J_{\mathrm{HH}}=7.1$ Hz, CH$_3$), 2.87(2H, ddd, $J_{\mathrm{HP}}=23$ Hz, $J_{\mathrm{HH}}=7.9$ Hz, $J_{\mathrm{HH}}=1.5$ Hz, PCH$_2$) 4.14(4H, quintet, $J_{\mathrm{HP}}=J_{\mathrm{HH}}=7.1$ Hz, OCH$_2$), 5.11(1H, ddt, $J_{\mathrm{HP}}=6.6$ Hz, $J_{\mathrm{HH}}=$ 7.9 Hz, $J_{\mathrm{HH}}=4.8$ Hz, -CH=), 5.30—5.42(1H, m, =CHO), 7.4—8.2(5H, m, arom)
3c	68	135—140/93	$C_{10}H_{19}O_5P$	47.87 (48.00	7.69 7.65	12.47 12.38)	1.32(6H, t, $J_{\mathrm{HH}}=7.1$ Hz, CH$_3$), 1.94(3H, dd, $J_{\mathrm{HP}}=5.1$ Hz, $J_{\mathrm{HH}}=1.2$ Hz, =CCH$_3$), 2.50(2H, dd, $J_{\mathrm{HP}}=21.7$ Hz, $J_{\mathrm{HH}}=7.6$ Hz, CH$_2$P), 2.16 (3H, s, COCH$_3$), 4.10(4H, quintet, $J_{\mathrm{HP}}=$ $J_{\mathrm{HH}}=7.1$ Hz, OCH$_2$), 5.06(1H, dtq, $J_{\mathrm{HP}}=6.5$ Hz, $J_{\mathrm{HH}}=7.6$ Hz, $J_{\mathrm{HH}}=1.2$ Hz, -CH=)
3d	56	160—164/26	$C_{15}H_{21}O_5P$	57.29 (57.69	6.77 6.78	10.15 9.92)	1.31(6H, t, $J_{\mathrm{HH}}=7.1$ Hz, CH$_3$), 2.07(3H, dd, $J_{\mathrm{HP}}=4.9$ Hz, $J_{\mathrm{HH}}=1.0$ Hz, =CCH$_3$), 2.59(2H, dd, $J_{\mathrm{HP}}=21.5$ Hz, $J_{\mathrm{HH}}=7.6$ Hz, CH$_2$P), 4.10 (4H, quintet, $J_{\mathrm{HP}}=J_{\mathrm{HH}}=7.1$ Hz, OCH$_2$), 5.20 (1H, $J_{\mathrm{HP}}=7.6$ Hz, $J_{\mathrm{HH}}=6.0$ Hz, $J_{\mathrm{HH}}=1.0$ Hz, CH=), 7.3—8.2(5H, m, arom)
4e	49	126—129/66	$C_{10}H_{19}O_5P$	48.24 (48.00	7.76 7.65	12.55 12.38)	1.33(6H, t, $J_{\mathrm{HH}}=7.0$ Hz, CH$_3$), 1.84(3H, dd, $J_{\mathrm{HH}}=1.6$ Hz, $J_{\mathrm{HH}}=3.0$ Hz, =CCH$_3$) 2.03(3H, s, COCH$_3$), 3.98(4H, quintet, $J_{\mathrm{HP}}=J_{\mathrm{HH}}=7.0$ Hz, OCH$_2$), 4.15—4.35(1H, m, OCH), 5.13—5.30(1H, m, HC=), 5.40—5.50(1H, m, HC=)
4f	48	123—125/66	$C_{10}H_{19}O_5P$	48.26 (48.00	7.50 7.65	12.51 12.38)	1.33(6H, t, $J_{\mathrm{HH}}=7.0$ Hz, CH$_3$), 1.75(3H, dd, $J_{\mathrm{HH}}=7.0$ Hz, $J_{\mathrm{HH}}=1.3$ Hz, =CHC$\underline{H}_3$), 2.13 (3H, s, COCH$_3$), 4.07(4H, quintet, $J_{\mathrm{HP}}=$ $J_{\mathrm{HH}}=7.0$ Hz, OCH$_2$), 4.38—4.40(1H, m, CHO), 5.59—5.64(1H, m, HC=), 5.85—5.90 (1H, m, HC=)
4g	65	160—163/39	$C_{15}H_{21}O_5P$	57.78 (57.69	6.71 6.78	9.86 9.92)	1.33(6H, t, $J=6.9$ Hz, CH$_3$), 2.17(3H, s, COCH$_3$), 4.18(4H, quintet, $J_{\mathrm{PH}}=J_{\mathrm{HH}}=6.9$ Hz, OCH$_2$), 5.84(1H, ddd, $J_{\mathrm{HP}}=15.0$ Hz, $J_{\mathrm{HH}}=7.4$ Hz, $J_{\mathrm{HH}}=1.0$ Hz, HCO), 6.02(1H, ddd, $J_{\mathrm{HP}}=7.3$ Hz, $J_{\mathrm{HH}}=16.0$ Hz, $J_{\mathrm{HH}}=5.3$ Hz, HC=), 6.78(1H, ddd, $J_{\mathrm{HP}}=4.8$ Hz, $J_{\mathrm{HH}}=$ 16.0 Hz, $J_{\mathrm{HH}}=1.0$ Hz, HC=), 7.2—7.5(5H, m, arom)

References

1) F. Ramirez, "Organo-Phosphorus Compounds, special lectures presented at the Symposium on Organo-Phosohorus Compounds held in Heidelberg, Germany, 1964," Butterworths, London (1964), p. 337.

2) M. Sekine, I. Yamamoto, A. Hashizume, and T. Hata, *Chem. Lett.*, **1977**, 485; D. A. Evans, K. M. Hurst, and J. M. Takacs, *J. Am. Chem. Soc.*, **100**, 3467 (1978).

3) A. N. Pudovik, T. K. Gazizov, Y. Y. Samitov, and T. V. Zykova, *Zh. Obshch. Khim.*, **37**, 706 (1967).

4) L. V. Nesterov, R. A. Sabirova, and N. E. Krepysheva, *Zh. Obshch. Khim.* **39**, 1943 (1969).

5) K. Sasse, "Methoden der Organischen Chemie, Organische Phosphorverbindungen Teil 2," ed by E. Müller, Georg Thieme Verlag, Stuttgart (1964), p. 113.